ELUCIDATION OF SONOCHEMICAL REACTION KINETICS OF BIODIESEL PRODUCTION FROM JATROPHA OIL

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ABSTRACT

Biodiesel, an alternative renewable fuel made from transesterification of vegetable oil with alcohol, is becoming more readily available for use in blends with conventional diesel fuel for transportation applications. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetables oils. Biodiesel production process is the transesterification of the used two-steps catalyzed process with jatropha oil and methanol, in the presence of alkali catalyst, to yield the ethyl ester as a product and glycerine as a by-product. In the acid treatment or the acid-catalyzed esterification, the temperature is set at 60°C, acid catalyst of 1% w/w H_2SO_4. These studies have been performed based on 2 effects, temperature and oil to methanol molar ratio with fixed parameter of 1% w/w NaOH and 20 kHz of frequency for optimization and lastly with time which is used for kinetic study. As a result, the best condition that has been determined for maximum biodiesel production was 1:6 of oil to methanol molar ratio. However, the temperature does not effect to the biodiesel yield. Biodiesel yield in biodiesel production from jatropha curcas oil were measured by using ^{1}H NMR spectrometer analysis. These processes which using ultrasonic reactor is easy and faster than other biodiesel production process because cavities caused by the ultrasound at the catalyst surface increase the catalyst activity and reduce the activation over potential loss.

ABSTRAK

Biodiesel, bahan bakar alternatif boleh diperbaharui yang terbuat dari pengtransesteran minyak sayuran dengan alkohol, menjadi lebih mudah sedia untuk digunakan dalam campuran dengan bahan bakar solar konvensional untuk aplikasi pengangkutan. Biodiesel adalah pengtransesteran dari dua digunakan-langkah proses mangkin dengan minyak jatropha dan metanol, dengan adanya mangkin alkali, untuk menghasilkan ester etil sebagai produk dan gliserin sebagai produk-oleh. Pada perlakuan acid atau pengesteran acidcatalyzed, suhu ditetapkan pada 60 °C, asid mangkin 1% w/w H_2SO_4. Pengajian-kajian ini telah dilakukan berdasarkan 2 kesan, suhu dan nisbah methanol untuk minyak dengan 1% pemangkin konsentrasi NaOH dan 20 kHz frekuensi untuk pengoptimum dan masa untuk pengajian kinetik. Akibatnya, keadaan terbaik yang telah ditetapkan untuk pengeluaran biodiesel maksimum adalah 1:6 nisbah minyak untuk methanol. Namun, suhu tidak membawa sebarang kesan terhadap penghasilan biodiesel. Biodiesel hasil dalam pengeluaran biodiesel dari minyak jatropha diukur dengan analisa dari alat ^{1}H NMR spectrometer.

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LIST OF ABBREVIATIONS

^{1}H NMR	Proton Nuclear Magnetic Resonance
ASTM	American Society for testing and materials
CO	Carbon monoxide
FFA	Free Fatty Acid
GC-FID	Gas Chromatography-Flame Ionized Detector
H_2SO_4	Sulphuric acid
JCO	Jatropha curcas oil
kHz	kilo hertz
MHz	mega hertz
NaOH	Sodium Hydroxide
NO_x	Nitrogen oxide
N_2O	Nitrous oxide
SO_x	Sulphur oxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide. Ever since energy demands have been steadily increasing along with the growth of human population and industrialization, it attracts the most attention because it is renewable, it can be used either pure or in blends with diesel fuel in unmodified diesel engine and it reduces some exhaust pollutants. Moreover, growing consumption of energy has rapidly depleted non-renewable sources of energy. Rising price of fossil-based fuels and potential shortage in the future have led to a major concern about the energy security in every country.

Biodiesel fuel is defined as alkyl esters of long-chain fatty acids (Knothe et al., 2002). It is produced in the alcoholysis or also known as transesterification reaction of natural triglycerides such as vegetable oil or animal fats with short-chain alcohol such as methanol or ethanol. The reaction requires the presence of base or acid catalysts, or enzymes, heating and efficient mixing, or it is conducted in non-catalytic but supercritical conditions. Base-catalyzed alcoholysis, as being much faster than acid-catalyzed, is mostly used commercially. Potassium and sodium hydroxide are usually used as a catalyst in the biodiesel production because of low price, ease handling in transportation and storage and the possibility to be prepared water-free. The main disadvantage of strong base alkaline hydroxides is the formation of undesired soaps in a direct reaction with esters and triglycerides. To counter the disadvantages, two-step transesterification is the best solution for preventing the formation of undesired soaps.

All feedstocks that consist of fatty acids or glycerol can be used for biodiesel production including jatropha oil. In European countries, rapeseed oil is used due to its widespread availability. Soybean oil is used in the Unites States of America, while palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. Feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.

1.2 PROBLEM STATEMENT

Energy is a basic requirement for every sector of economic development in a country. As a result, the growth of industries, transport, agriculture and other human needs depends hugely on the petroleum fuels. In the recent years, the fossil fuel resources are depleting rapidly with consequent environment degradation. Being a fast solution to the shortage of liquid fuel, biodiesel is one of the most popular alternatives of all time. This research seeks to solve this uncertainty in the feedstock sustainable selection, of the types of biodiesel feedstock, namely Jatropha oil.

Ultrasonic transesterification in biodiesel production can reduce its processing time. Years before, conventional agitation has been used for producing biodiesel with requirement time up to 12 hours. With ultrasonic method, the processing time of biodiesel yield only take less than 60 minutes. The requirement of catalyst also reduced by 50% due to the increased chemical activity in the cavitations formed due to sonication. Moreover, the amount of excess alcohol required also reduced abundantly while increasing the purity of the glycerine formed.

1.3 OBJECTIVES

The objective of this research was to prepare biodiesel by sonochemical methods which are using two-step transesterification with ultrasonic aid, alkali catalyst sodium hydroxide and acid catalyst of sulphuric acid. Second objective is to optimize reaction condition for biodiesel production from jatropha oil with the temperature and molar ratio of oil to methanol as the manipulated parameters. The third objective is to study the sonochemical reaction kinetics of biodiesel production from jatropha oil.

1.4 SCOPE OF STUDY

1.4.1 To compare the effect of temperature, molar ratio of oil to methanol, and frequency of ultrasonic on the yield of biodiesel from jatropha oil using ultrasonic transesterification.

1.4.2 To study the sonochemical kinetics based on the yield of biodiesel from jatropha oil.

1.4.3 To analyze the product using Nuclear Magnetic Resonance (^{1}H-NMR).

1.5 RATIONALE AND SIGNIFICANCE

The rationale of this proposed research project is to provide experiential evidence to compare the purity and yield of jatropha biodiesel. The outcome of this research would denote the identification of a feedstock for biodiesel production that is accomplishable, sustainable and efficient in Malaysia. The classification of this feedstock will be a basis for biodiesel yield on an industrial scale to counter the current global shortage of fossil fuel.

The big advantages of using ultrasonic transesterification would bring about amount of significance in the biodiesel production industry. This is because aside from giving relatively high yield, it would significantly reduce the length of processing time needed for production, and this will eventually goes well to supply the highly increasing rate of demand for alternative liquid fuel. With this method, biodiesel production industry in Malaysia would be able to provide the needs of Malaysian at a rapid rate, hence dismissing the dependence on foreign alternative fuel that may arise in the future. As a result, Malaysian fuel crisis could be deal at an optimal rate by using its abundant feedstock resources and ultrasonic transesterification.

CHAPTER 2

LITERATURE REVEW

2.1 INTRODUCTION

Fossil-based fuels have many disadvantages such as atmospheric pollution and environmental issues. Fossil fuels emissions are top contributors of greenhouse gases which may lead to global warming. Combustion from fossil fuels is major source of air pollutants, which consist of CO, NO_x, SO_x, hydrocarbons, particulates and carcinogenic compounds. Based on the report, 17 major oils and fats world production are 100 billion tones and out this 79% are from vegetable oil (Hamn and Hamilton, 2002).

This has attracted to research, development and application of vegetable based oil in industrial and automotive sectors which has rapidly increasing. Currently, diesel-powered vehicles represent about one-third of vehicles sold in Europe and United States (Jayed et al., 2009). The global consumption of petroleum diesel is 934 million tonnes per year (Kulkarni and Dalai, 2006). Biodiesel is one of the most assuring alternative fuels for diesel engines. The arrogation of biodiesel has significantly increased from 2005 especially in USA (Pahl, 2008). There are several advantages of biodiesel as compared to fossil diesel. Among of it is (1) It helps to reduce carbon dioxide and other pollutants emission from engines, (2) Engine modification is not needed as it has familiar properties to diesel fuel, (3) It comes from renewable sources whereby people on grow their own fuel, (4) Diesel engine performs better in biodiesel due to a high cetane number, (5) High purity of biodiesel would eliminate the use of lubricant, (6) Biodiesel production is more efficient as compared to fossil fuels as there will be ni underwater plantation, drilling and refinery and (7) Biodiesel would make an area become independent of its need for energy as it can be produced locally (Jain and Sharma, 2010; Jayed et al., 2009; Nie et al., 2006; Robles-Medina et al., 2009; Shah et al., 2004; Su and Wei 2008; Vieira et al., 2006).

During the year of 1997, the production of biodiesel fuel was 550,000 tones in Europe, 10,000 tones in Malaysia and 9000 tones in North America. In 2000, the yearly production of biodiesel in Europe was 1,210,000 tones. The production has increased 2.2 times in three years time (Kann *et al*, 2002).

2.2 BIODIESEL

Today, biofuel is at the most priority of the array of alternative energy sources that are being researched and developed. With similarity of physical and chemical properties that are compatible with its fossil counterpart, biodiesel has placed as one of the most appropriate alternative to complement, and might even substitute fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modification, and to form blends with fossil diesel make it the most feasible alternative energy source to invest in.

The major aspect of life cycle assessment that biodiesel serves to benefit the environment more than fossil fuel is the potential of global warming, known as carbon dioxide, CO_2. CO_2 produce during the process of fuel production, biological based and fossil based like. Since that biodiesel mainly consists of renewable material, one could expect a large saving of greenhouse gases compared to conventional fuel. While the case of CO_2 still consider true, certain sides argue if other greenhouse gases like N_2O and CH_4 are considered, which contribute to a higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7 kg of saved CO_2 equivalent for every kg of substituted fossil diesel fuel. Most biodiesel fuels inherently contain little or no sulphur; this eventually reduces sulphur dioxide exhaust from diesel engines to virtually zero.

2.2.1 CHARACTERISTIC OF BIODIESEL

Biodiesel is an alternative diesel fuel, form chemically by renewable biological sources such as vegetable oils and animal fats with an alcohol to accelerate the reaction (Leung et al, 2006). It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial (Krawczyk, 1996).

Figure 2.1 shows an example of biodiesel. Its colors cab is varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~150°C (300°F), making it rather non-flammable. Biodiesel has density of ~0.88g/cm3, less than water. Biodiesel that unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petro-diesel that produces from petroleum.

Moreover, biodiesel is also environmental friendly burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It adapts in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable

2.3 TRANSESTERIFICATION

Transesterification, also called alcoholysis, is the reaction of a fat or oil with an alcohol with an alcohol to form esters and glycerol. It is the displacement of alcohol from an ester by another alcohol which is similar to hydrolysis process except that alcohol is used instead of water. Each reaction step is reversible. A catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side.

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms (Sprules and Price, 1950). Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages which is polar and shortest chain alcohol. It can rapidly react with triglycerides and sodium hydroxide is easily dissolved in it.

Figure 2.2 shows the overall reaction of transesterification process which consist of three consecutive steps; the triglyceride is converted to diglyceride, monoglyceride and finally glycerol. A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol. The excess amount of alcohol is commonly more suitable to boost the reaction towards the desired final product (Marchetti et al, 2007).

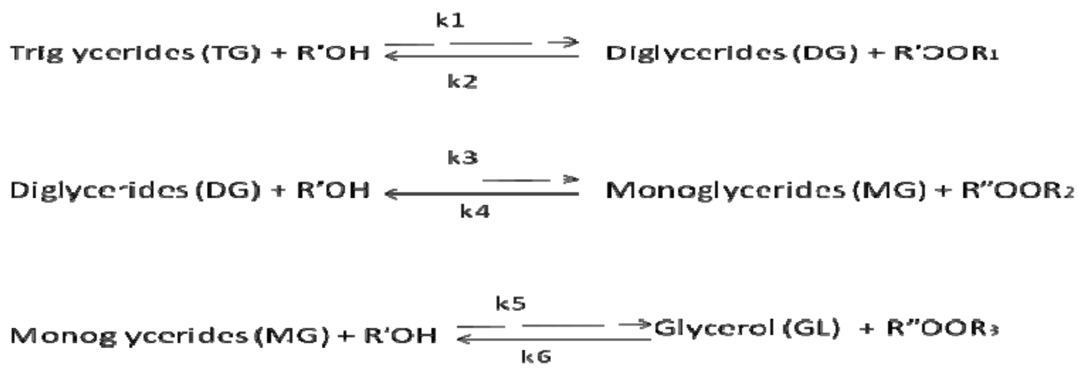

Figure 2.2: Consecutive steps of transesterification

2.4 GLYCERINE WASHING AND METHANOL RECOVERY PROCESS

Glycerine is a byproduct of transesterification reaction between oil and methanol. This glycerine will be separated out of the product and the methanol recovery. A considerable amount of alcohol can be discovered for reuse since the methanol used excessively to allow for the transesterification. To recover alcohol, vacuum evaporation, distillation, and water washing are among available method. An efficient method of methanol removal would be the vacuum evaporation since it evaporates the alcohol within its boiling point and recovers all. The glycerine can be removed from the product by decantation.

2.5 GLYCERINE

Glycerine or also known as glycerol is a simple polyol which is formed as a byproduct of the production of biodiesel through transesterification process. It is a colourless, odourless, viscous liquid that is widely used in pharmaceutical formulations. It has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature (Subramanian *et al.*, 2000).

2.6 ALKALI CATALYST

The common catalyst applied during alkaline transesterification at industrial level application includes the homogeneous catalysts such as sodium hydroxide, potassium hydroxide, etc.

The benefits homogeneous catalyst such as sodium hydroxide and potassium hydroxide has been efficient at industrial level for the biodiesel yield. However, the biodiesel and glycerol produced have to be purified to remove the catalyst and need to wash with hot distilled water twice or thrice.

Producing alcoxy before the reaction is a best move to gain a better global efficiency. The alcoxy reaction is

$$R_2CH_2OH + NaOH \rightarrow H_2O + R_2CH_2ONa$$

The amount of catalyst that should be added to the reactor varies from 0.5 to 1 % w/w. The alkali process is more efficient and less corrosive than the acid process (J.M. Marchetti et al., 2003).

2.7 ACID CATALYST

Acid catalyst is used for acid catalyzed transesterification which the amount of free fatty acid content in the oil is high. Sulfuric acid, sulfonic acid and hydrochloric acid are common used as acid catalyst.

Despite of the fact that acid catalyst can used to produce biodiesel with high free fatty acid content oil, acid catalysts have been neglected due to slow reaction rate. However, it is still being used to lower its free fatty acid content before alkali transesterification process. The amount of catalyst that should be added to the reactor varies from 0.5 to 1% (Song *et al.*,2007).

2.8 AMOUNT OF CATALYST

Three different homogeneous catalysts which is sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxde (CH_3ONa) shows the same pattern on the alkali transesterification but different amount of catalyst will required to achieve the same conversion (Leung *et al*, 2006). The optimum requirement of the catalyst were 1.1, 1.3, 1.5 wt% for NaOH, CH_3ONa, and KOH respectively for the maximum ester content production. The amount of NaOH required was less than the amounts of both CH_3ONa and KOH for the same conversion of methyl ester as NaOH has lower molar mass (40 g/mol), compared to CH_3ONa has 54 g/mol and KOH with 56 g/mol.

In contrary, in terms of yield, CH_3ONa proved to be better than NaOH and KOH due to no water was form as side product since CH_3ONa dissociates into CH_3O^- and Na^+. Meanwhile, NaOH and KOH forms sodium or potassium methoxide when dissolved in methanol and forms water as side product. This side product will then reacts with Na^+ (or K^+) to form soaps with the saponification reaction of triglyceride leading to the reduction of final product yields.

$$CH_3OH + NaOH \text{ (or KOH)} \rightarrow CH_3ONA \text{ (or } CH_3OK) + H20$$

2.9 ULTRASONIC TRANSESTERIFICATION

In the ultrasound-assisted transesterification, the formation, growth and implosive collapse of micro bubbles known as ultrasonic cavitation induced acoustically in the bulk of the liquid phase increase the mass transfer between the two phases by equip both heating and mixing (J.Ji, 2006). Cavitation causes a localized increase in temperature at the phase boundary and supplies the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction.

The collapse of the cavitation bubbles disrupts the phase boundary and cause emulsification by ultrasonic jets that affect one liquid to another. These effects speed up the transesterification reaction rate and shorten time required, while high final yields of biodiesel are commonly achieved.

When the reaction is carried out via ultrasonic wave, transesterification is efficiently mobilized, with short time required. As the result, a drastic reduction in the quantity of by-product and a short separation time is obtained and at the same time can reduce the energy consumption. Biodiesel is primarily produced in the batch processes, in which a basic homogenous catalyst is introduced to catalyze the reaction. Ultrasound allows for the continuous processing. Besides reducing the reaction time, ultrasonication also reduces the separation time compared to the conventional agitation method.

When using the ultrasonication, the amount of excess alcohol required can be reduced. Most commonly, the sonication is performed at an elevated pressure (1 to 3 bar, gauge pressure) using a feed pump. Industrial biodiesel processing does not require much ultrasonic energy. In addition, ultrasonication is an effective means to increase the reaction speed and conversion rate in the commercial processing.

Figure 2.3 shows the typical result of the transesterification of rapeseed oil with potassium hydroxide studied by Carmen Stavarache. The blue line is the control sample, was exposed to intense mechanical mixing while the red line represent the sonicated sample with respect to the volume ratio, catalyst concentration and temperature. The horizontal axis shows the time after mixing or sonication, respectively. The vertical axis shows the volume of glycerin that settled at the bottom. This is the simple means of measuring the reaction speed. In this diagram, the sonicated sample (red line) reacts much faster than the control sample (blue line).

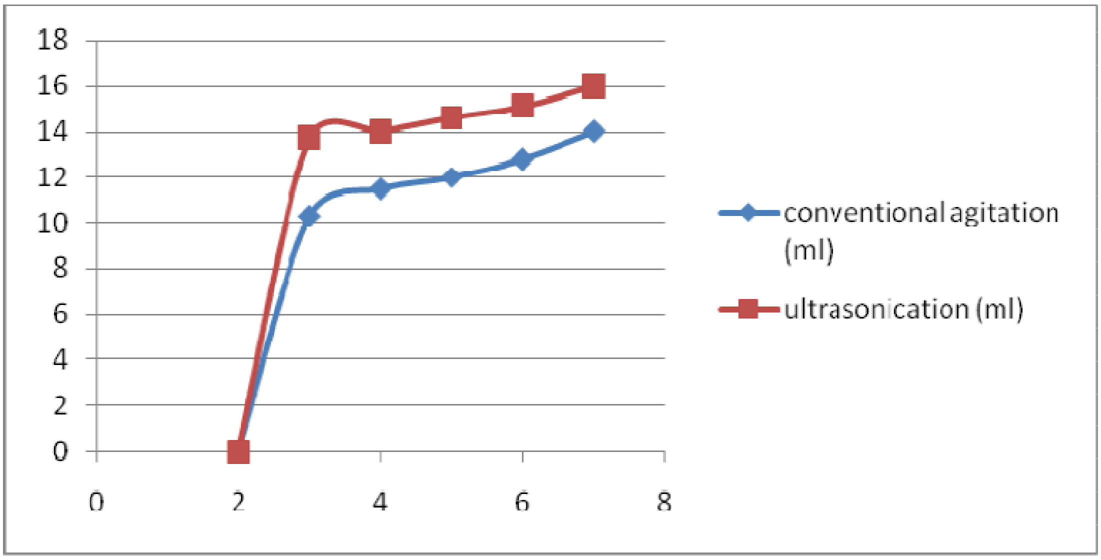

Figure 2.3: Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication